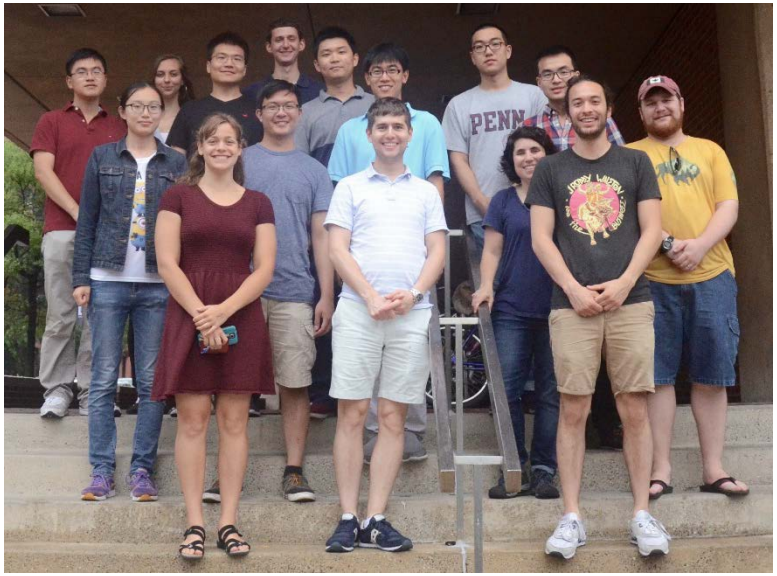
Role of Surface Chemistry on Charge Carrier Transport in Quantum Dot Solids

Cherie R. Kagan, University of Pennsylvania
in collaboration with the Murray group

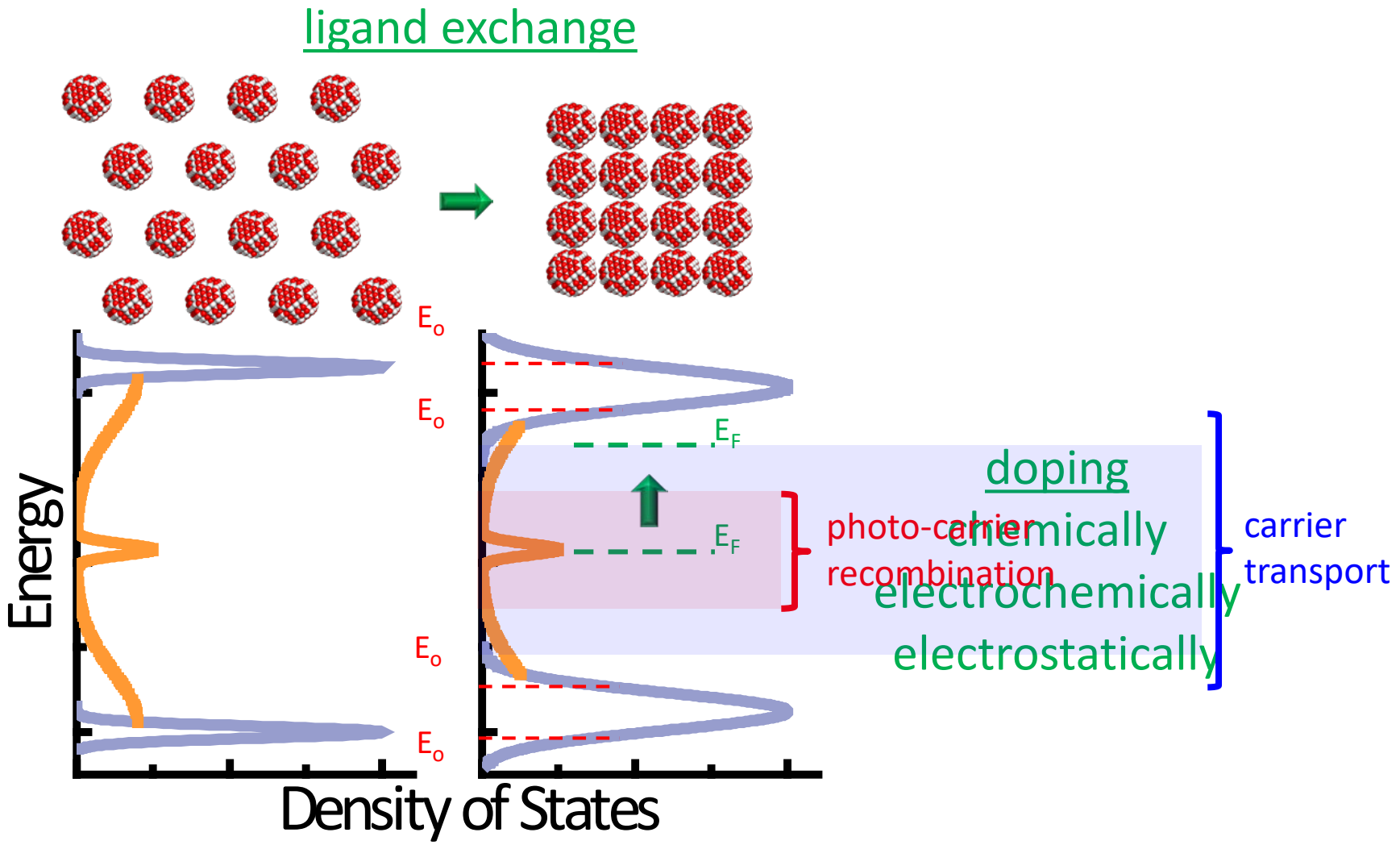


U.S. DEPARTMENT OF ENERGY | Office of Science

NSF

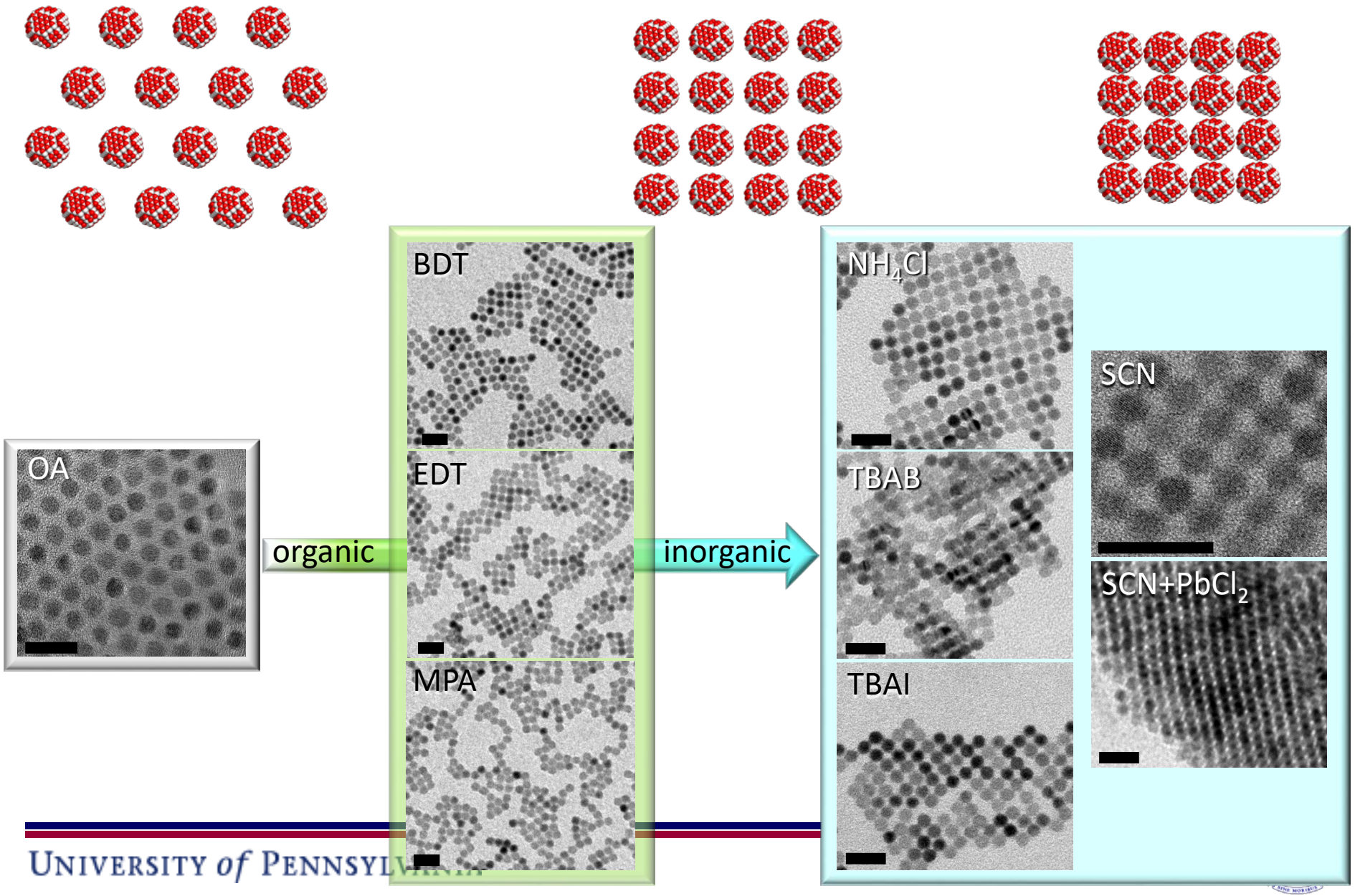
EFRC CASP

Density of Electronic States in Quantum Dot Solids

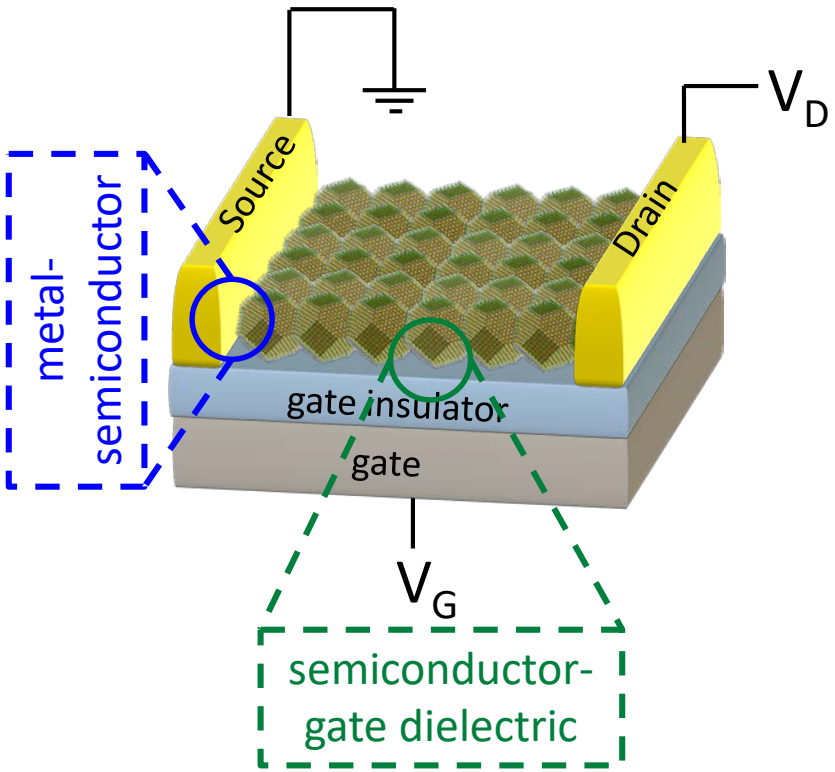


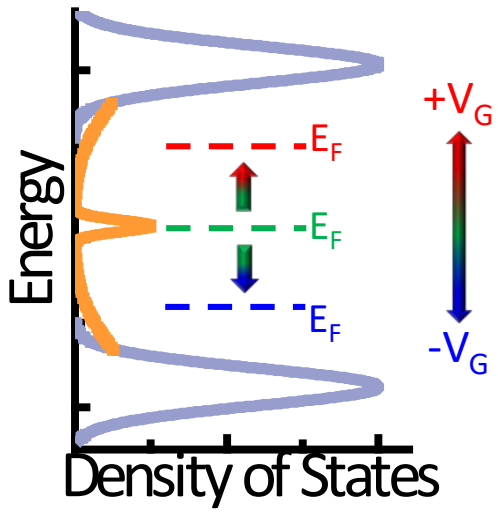
Kagan, Murray, Nat. Nano ***10****, 1013 (2015)*

Examples of Ligand Exchange in Pb-Chalcogenide Quantum Dot Solids



Field-Effect Transistor Measurements

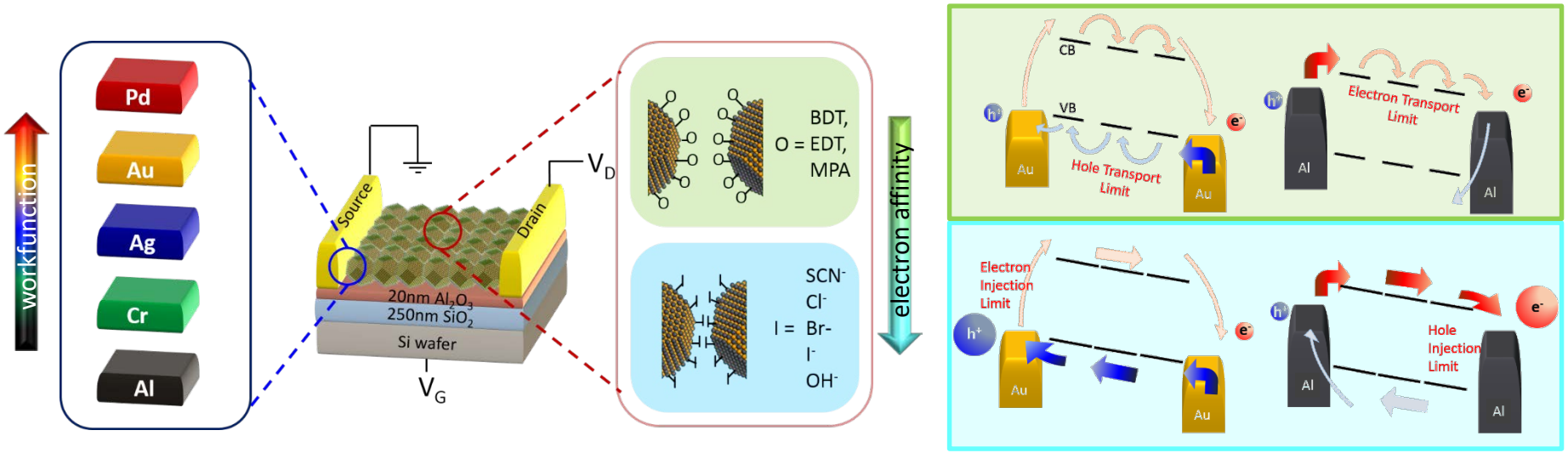




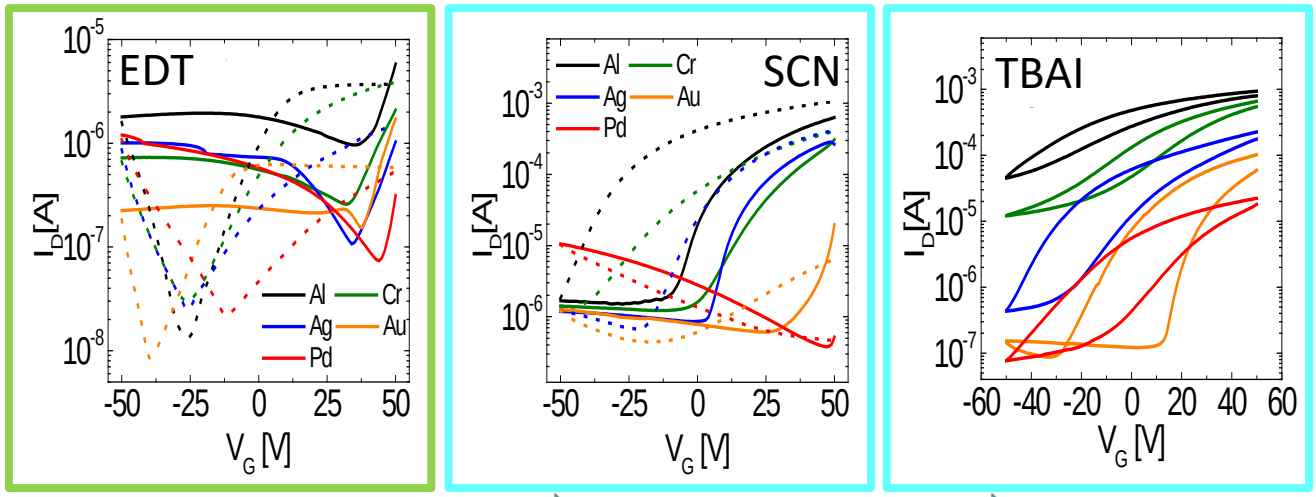
$$\Delta n \text{ or } \Delta p \propto \frac{(V_G - V_T)C_{OX}}{q}$$

- metal-semiconductor and semiconductor-gate oxide interfaces affect measurements
- induced carrier concentration depends on the gate voltage shifting the quasi-Fermi level

Charge Injection and Transport in PbSe Quantum Dot FETs



- charge injection and transport control the polarity and magnitude of the current



coupling → ligand

Oh, Wang, Berry, Choi, Zhao, Gaulding, Paik, Lai, Murray, Kagan, Nano Lett ***14****, 6210 (2014).*

Stoichiometric Control of Pb-Chalcogenide Thin-Film QD Solids

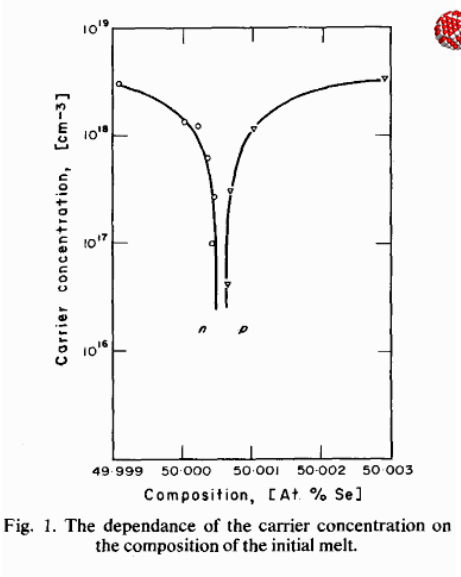
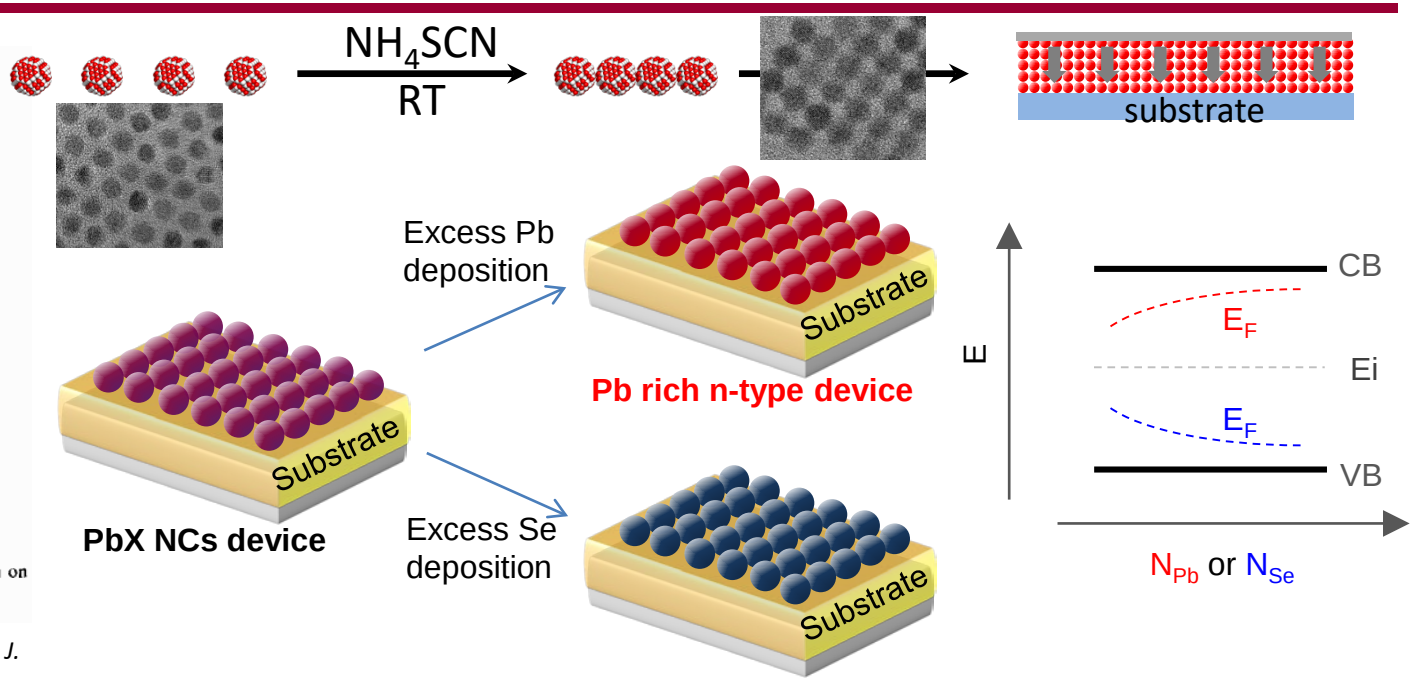
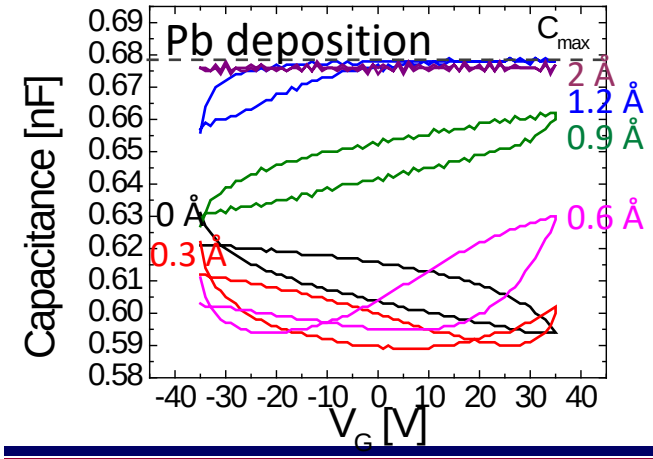
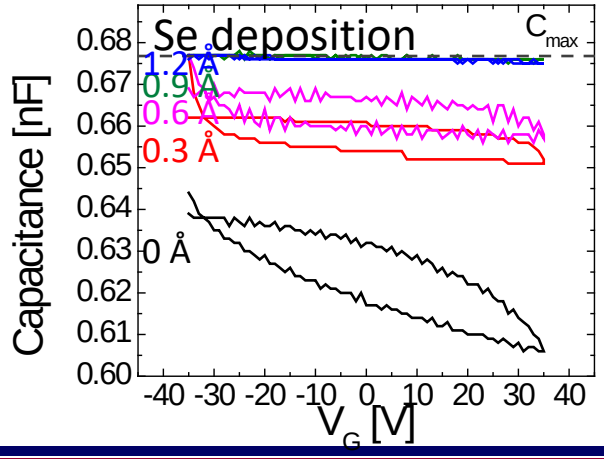


Fig. 1. The dependance of the carrier concentration on the composition of the initial melt.

U. SCHLICHTING and K. H. GOBRECHT, *J. Phys, Chem. Solids, 1973, 34, 753*



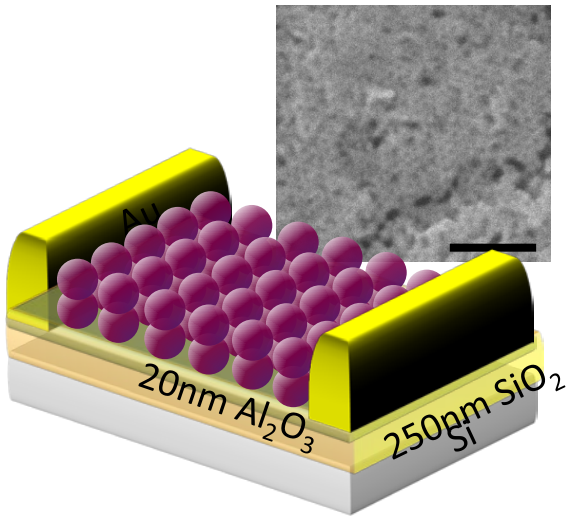


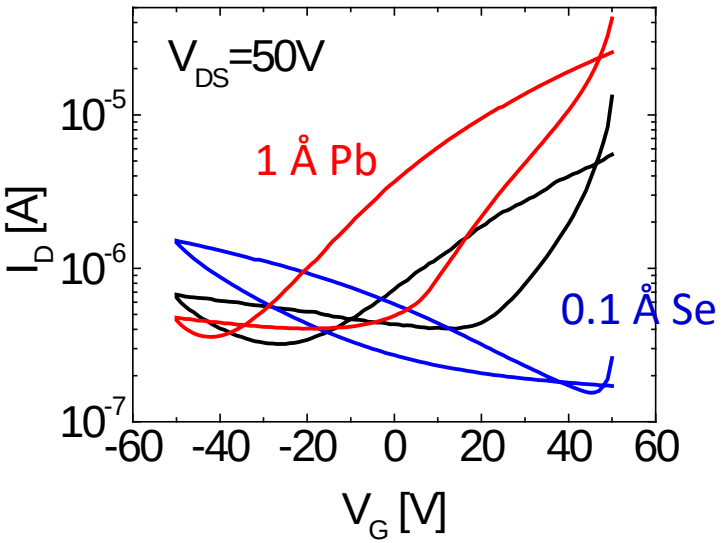


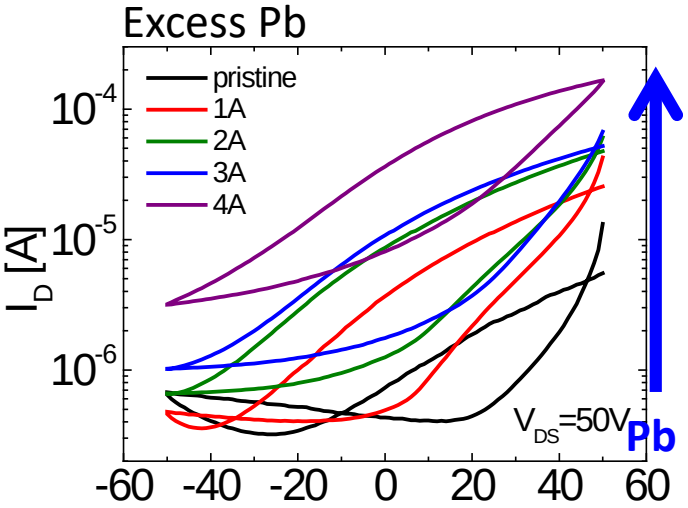
controlled carrier concentration over the range of $10^{15}/cm^3$-$10^{20}/cm^3$

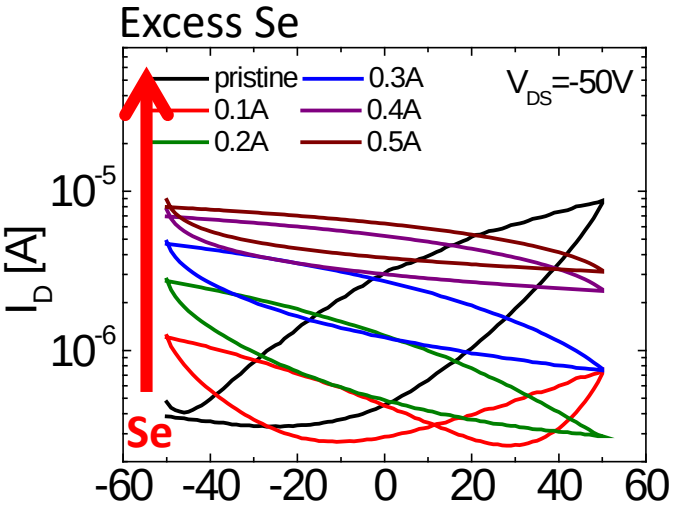
*Oh, Berry, Choi, Gaulding, Paik, Hong, Murray, Kagan, ACS Nano **7**, 2413 (2013)*

Case Study: Stoichiometric Control of Carrier Statistics in Pb-chalcogenide Quantum Dot Thin Films





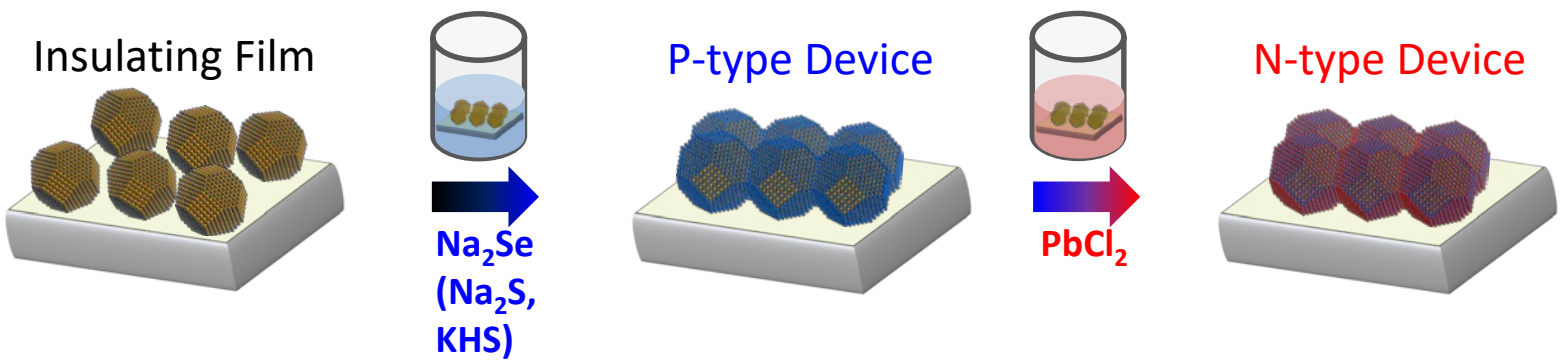


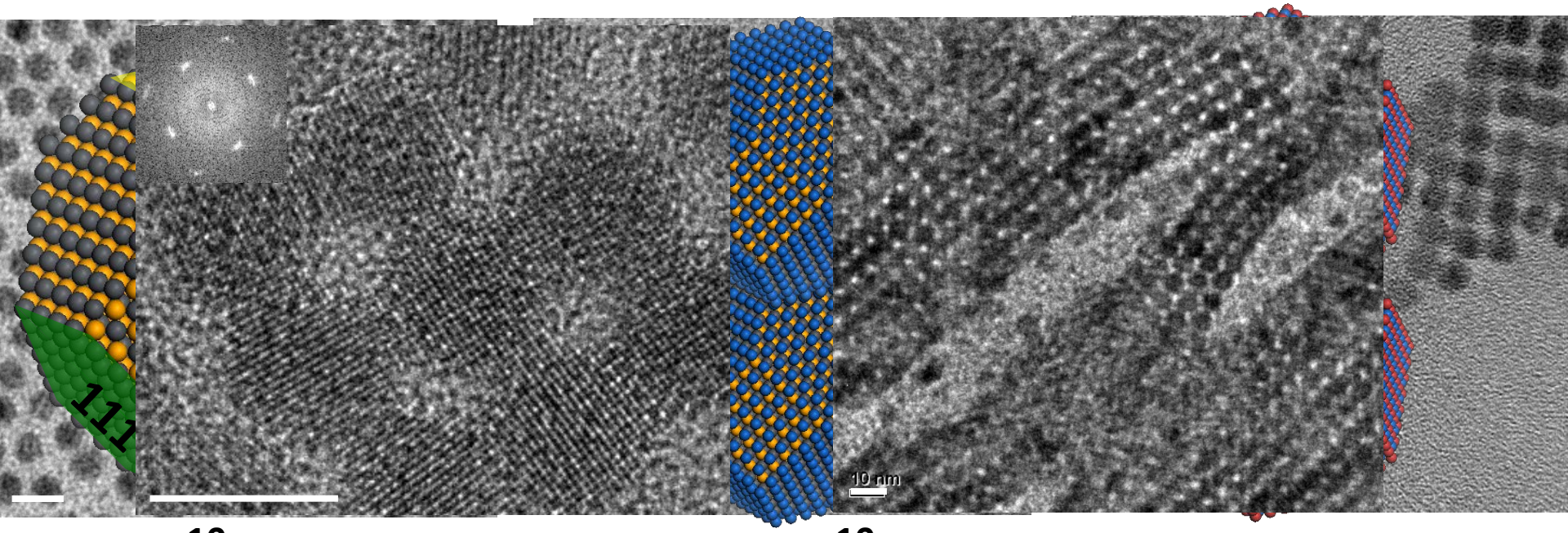


At 2-3 Å Pb, μ_e~10 cm^2/Vs

At 0.2-0.3 Å Se, μ_h~0.5 cm^2/Vs

Solution-based Stoichiometric Control of PbE (E=S, Se) Quantum Dot Thin Films





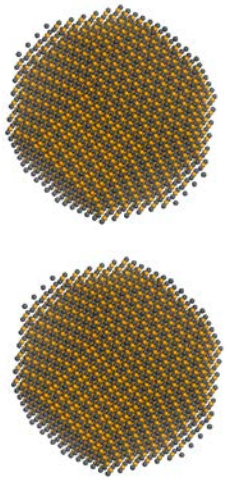
10nm **10nm** **10nm**

hexagonal to square ordered assemblies driven by high chalcogen surface energy

akin to ligand stripping by Vanmaekelbergh, Hanrath ..
Oh, Berry, Choi, Gaulding, Lin, Paik, Diroll, Muramoto, Murray, Kagan, Nano Lett ***14****, 1559 (2013).*

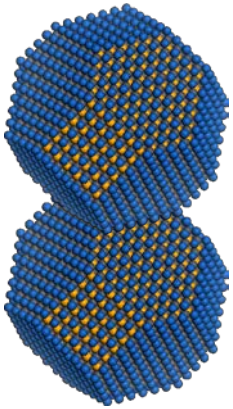
Stoichiometry Change

As-synthesized NCs



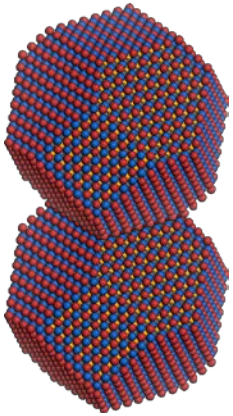
Na_2Se (Na_2S, KHS)

Chalcogen-rich NCs



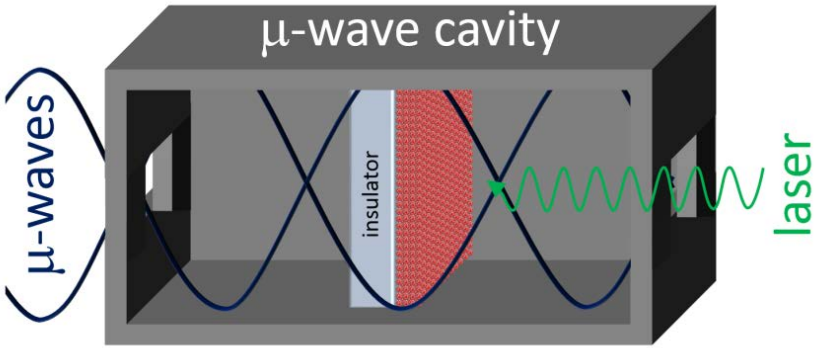
$PbCl_2$

Lead-rich NCs

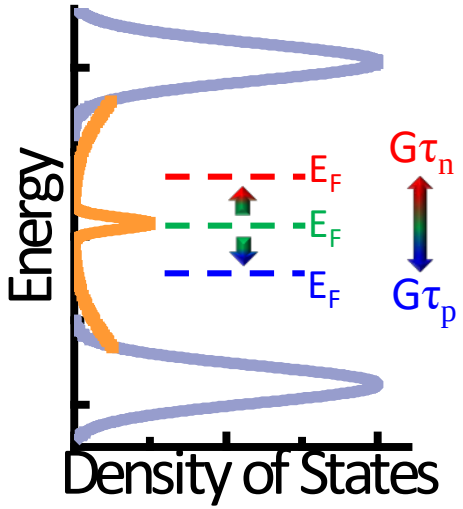


As-synthesized NCs		Chalcogen-rich NCs		Lead-rich NCs
No. of Pb atoms : 2190	=	No. of Pb atoms : 2190	< (+560)	No. of Pb atoms : 2754
No. of Se atoms :1925	< (+620)	No. of Se atoms : 2558	=	No. of Se atoms : 2558
Pb:Se (model)=1.137:1	→	Pb:Se (model)=0.847:1	→	Pb:Se (model)=1.065:1
Pb:Se (by ICP)=1.145:1		Pb:Se (by ICP)=0.841:1		Pb:Se (by ICP)=1.073:1

Flash-Photolysis, Time-Resolved Microwave Conductivity



generation rate, G

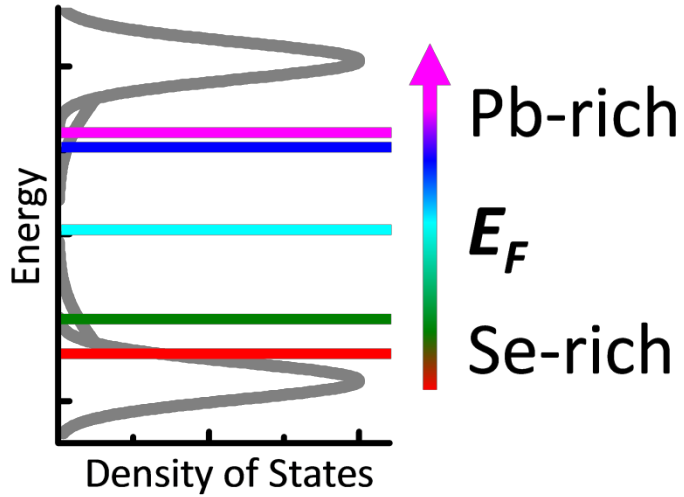


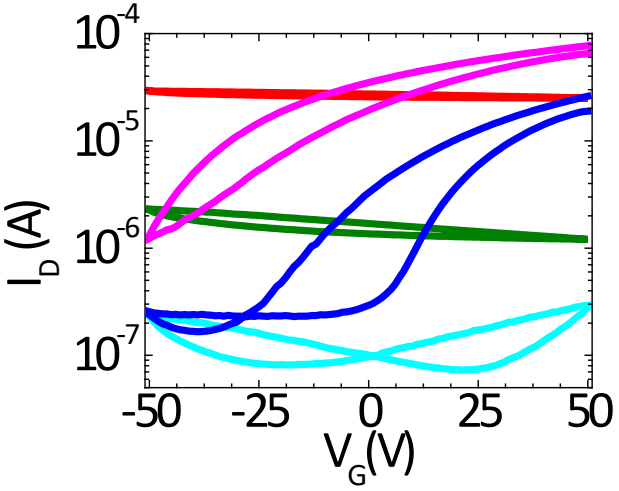
$\Delta n,p = G\tau_{n,p} \longrightarrow 0$ at low intensity

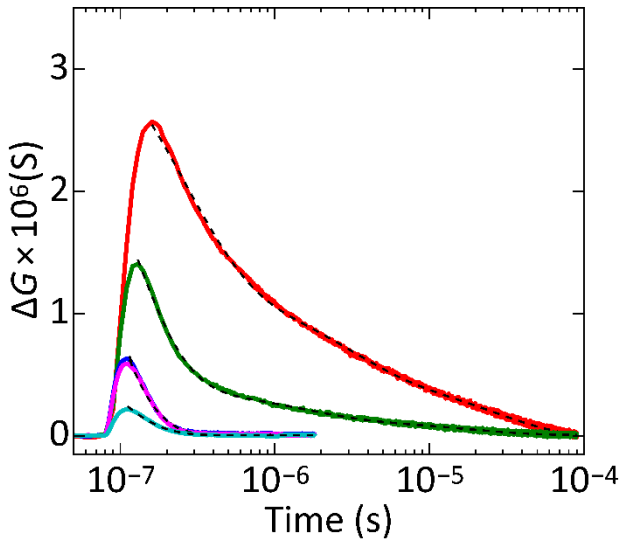
- contactless
- Fermi energy unaltered by measurement, particularly at low intensity
- time-resolution limited by cavity response and microwave frequency in the ns-μs

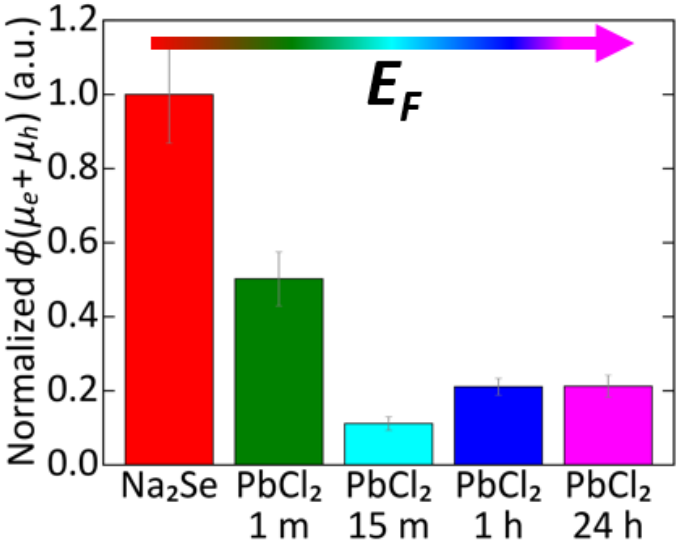
Goodwin, Straus, Gaulding, Murray, Kagan, Chemical Physics, ***471*** *81-88 (2016)*

TRMC Measurements of Doped PbSe Quantum Dot Thin Films







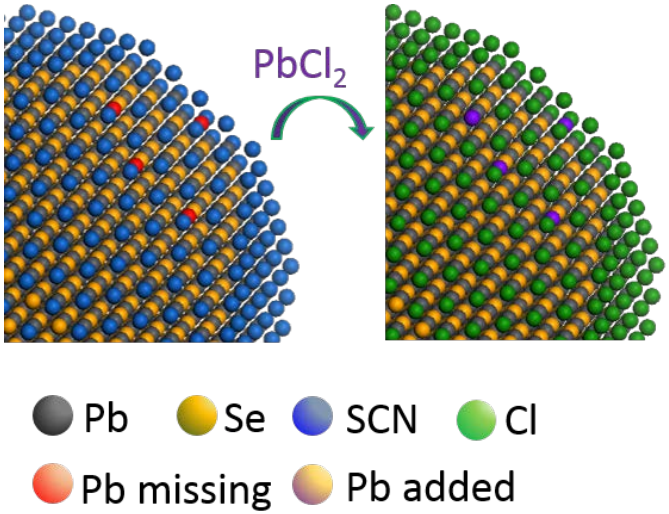


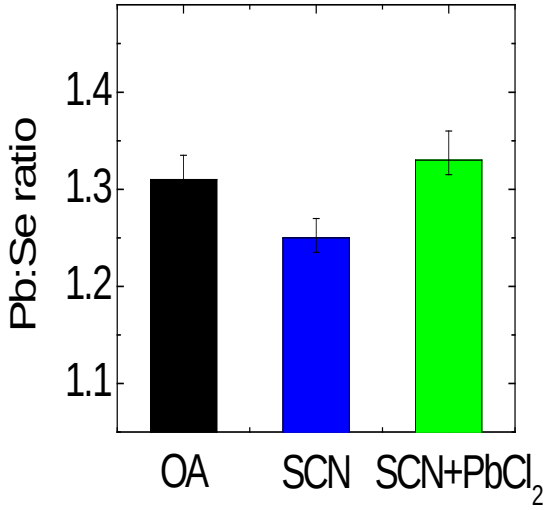
- carrier mobility increases as Fermi level approaches the band edges

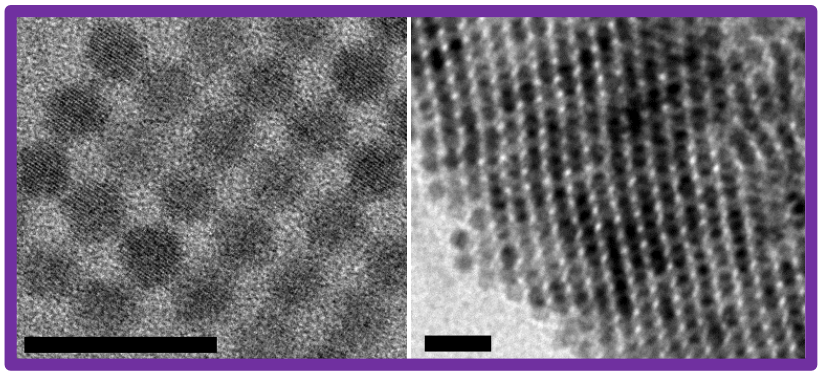
Quantum Dot Surface Repair in IV-VI Materials

solvents and ligand exchange processes strip atoms from the quantum dot surface

Owen, Hens, Sargent, …

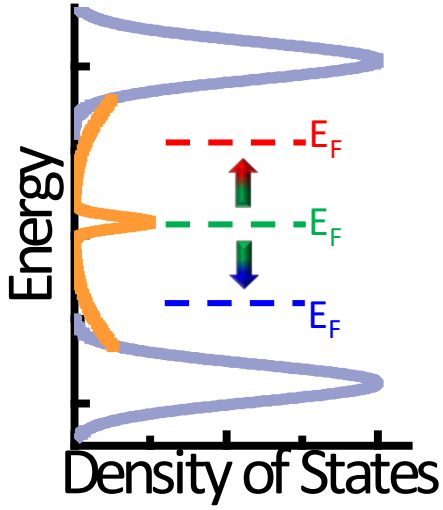


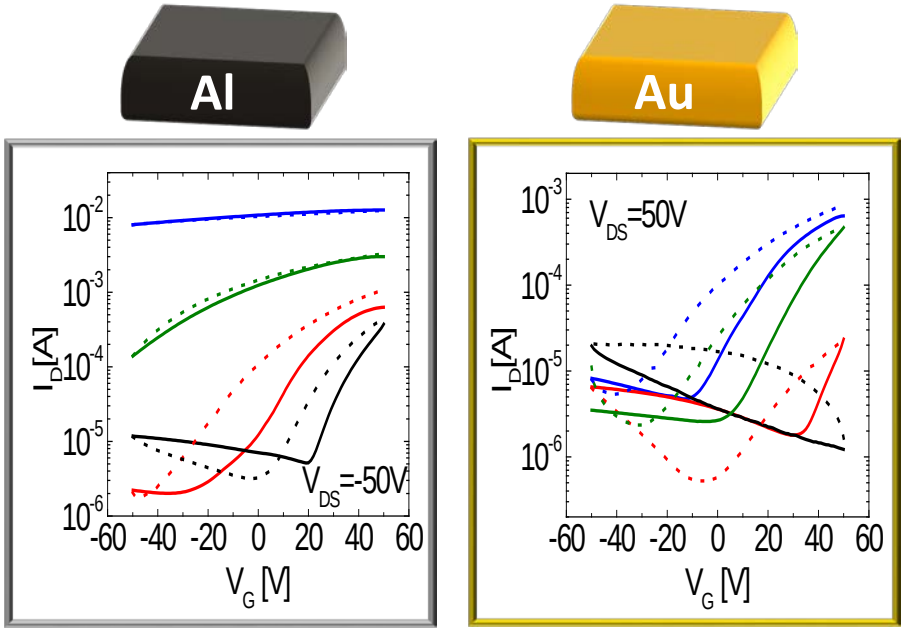




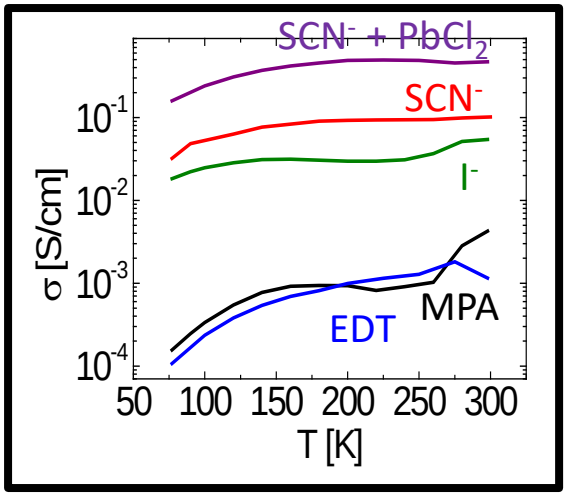
*Oh, Wang, Berry, Choi, Zhao, Gaulding, Paik, Lai, Murray, Kagan , Nano Lett **14**, 6210 (2014)*
*Goodwin, Diroll, Oh, Paik, Murray, Kagan , J. Phys. Chem C **118**, 27097 (2014).*

Coupling and Carrier Concentration Dependent Transport in PbSe Quantum Dot FETs

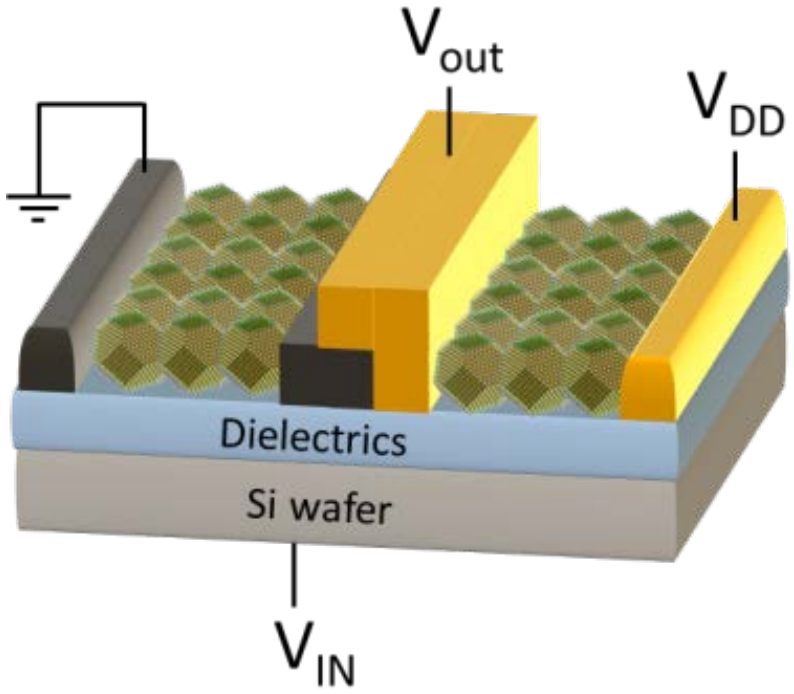


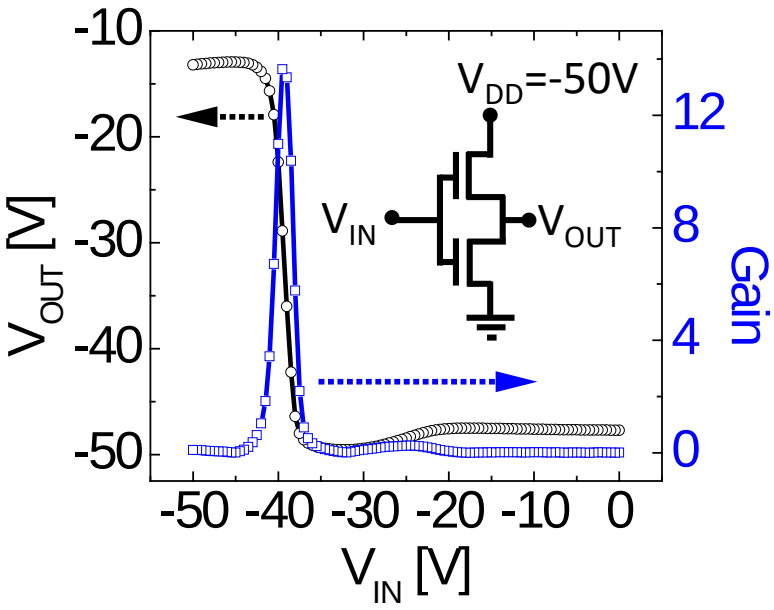


as electron concentration increases through chemical or electrostatic doping or charge injection, transport transitions from hopping to more extended state

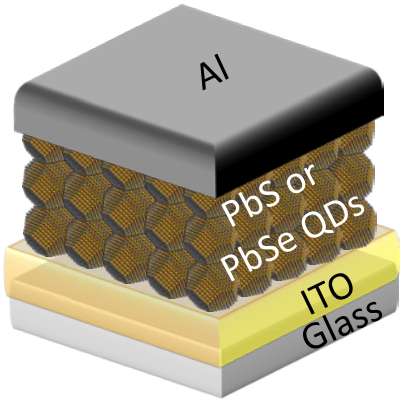


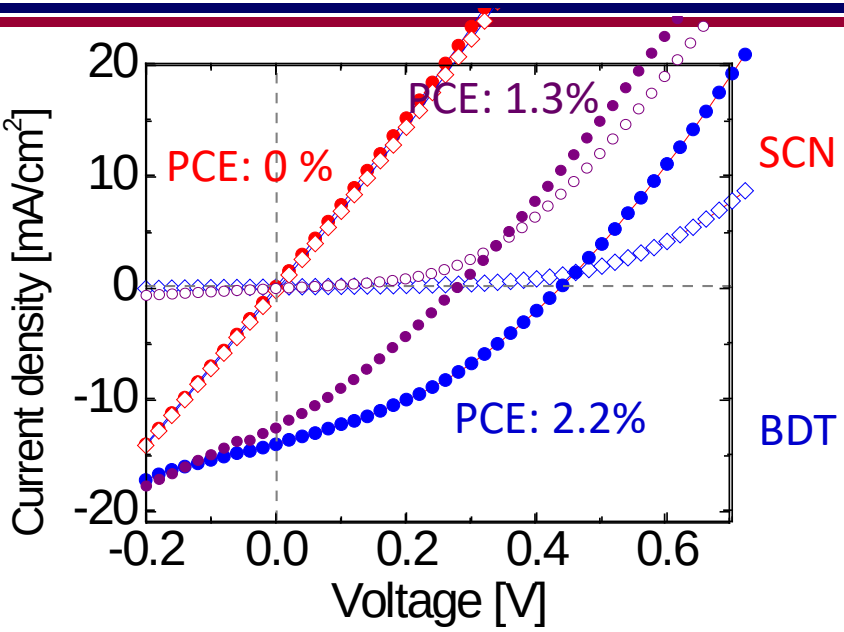
Integrated Quantum Dot CMOS Inverter





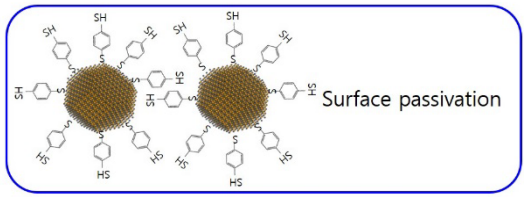
Can Solar Cells Be Fabricated from Strongly-Coupled NCs?

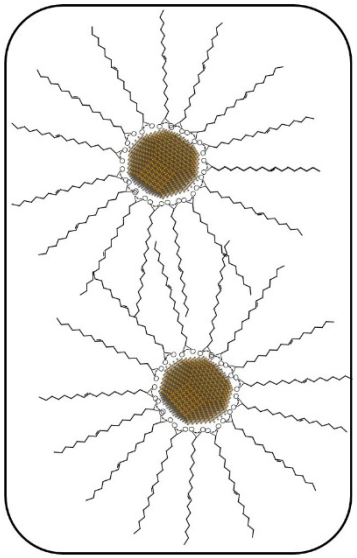




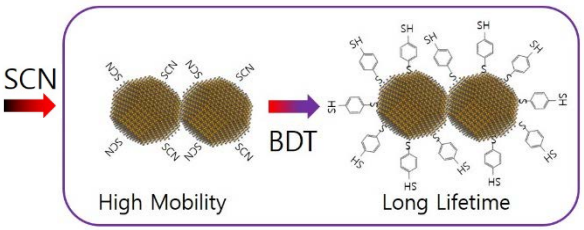
SCN

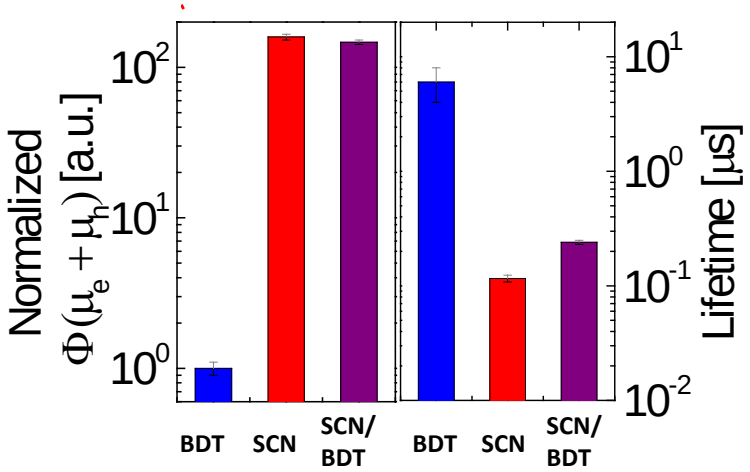
BDT





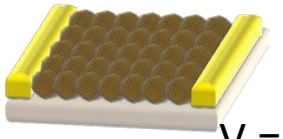
Hybrid Exchange

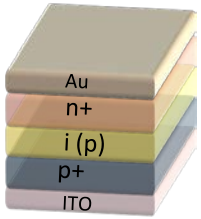


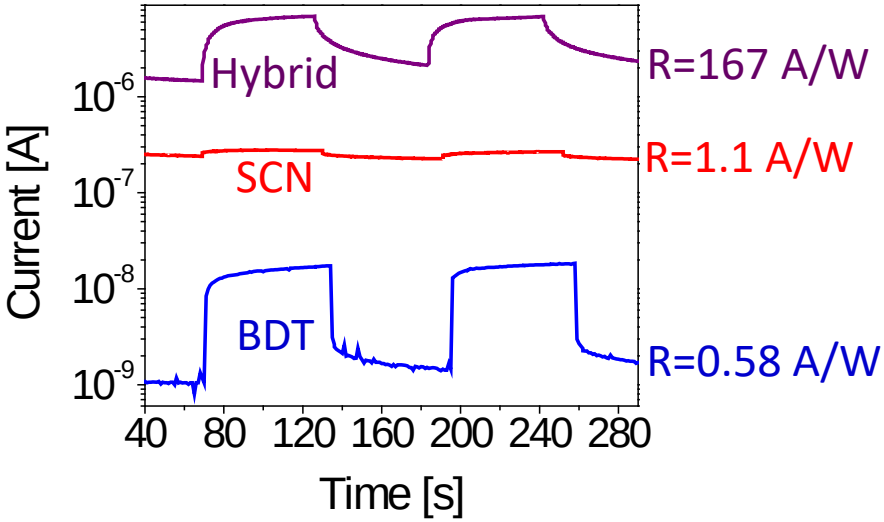


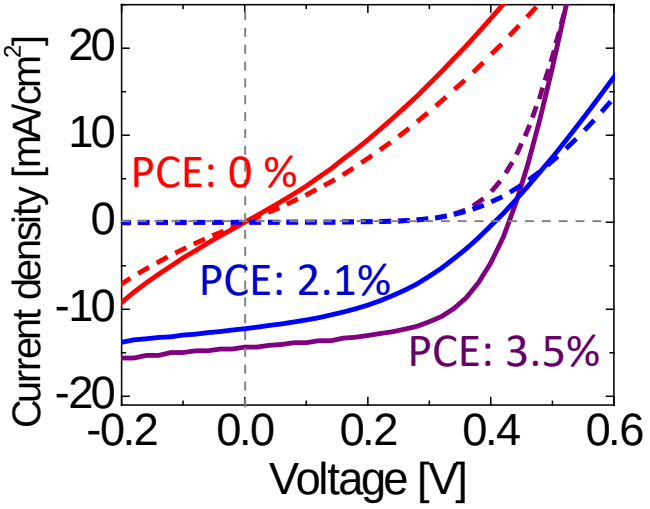
Oh, Straus, Zhao, Choi, Lee, Gaulding, Murray, Kagan, Chem Comm, ***53*** *728-731 (2017).*

Photoconductors and Photodiodes



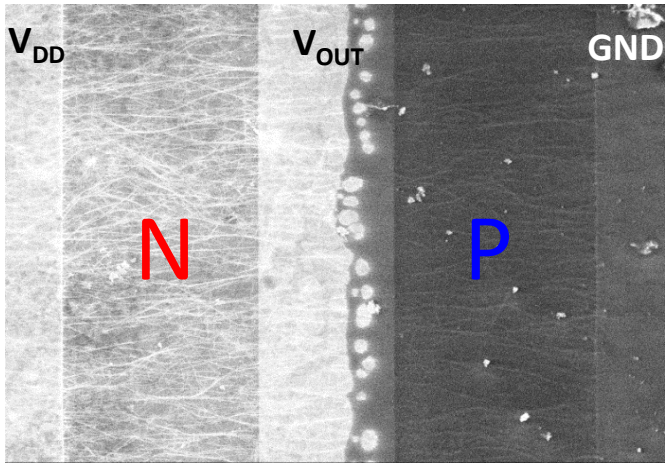


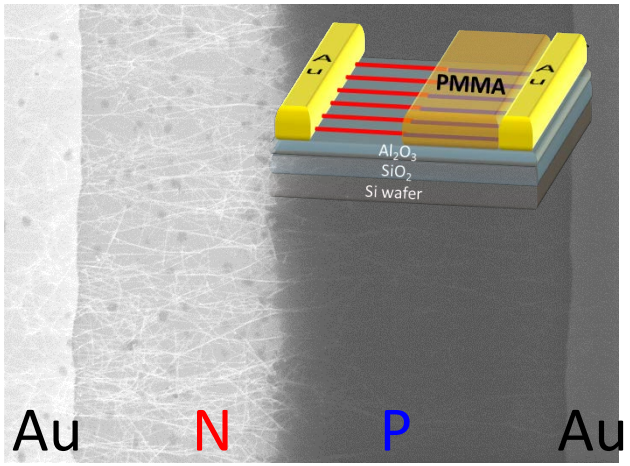


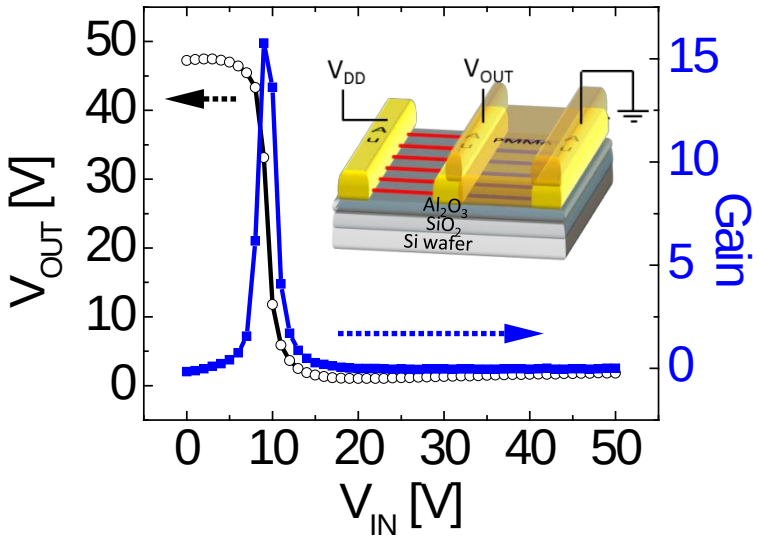


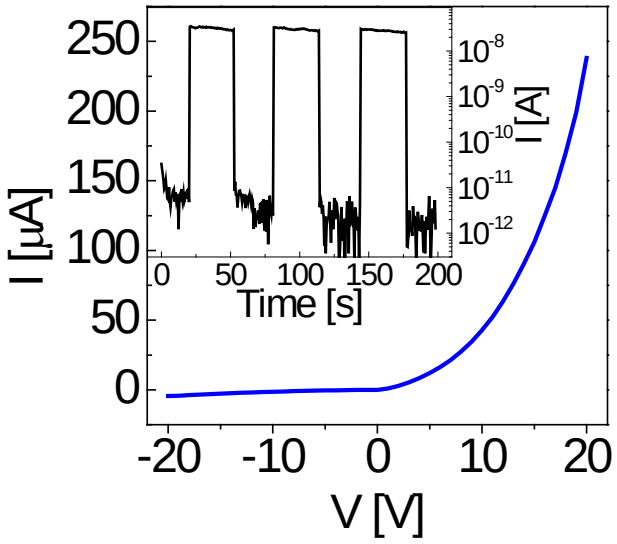
Avenue to realize high carrier mobility (>1 cm^2/Vs), long carrier lifetime QD materials for optoelectronics?

Surface Engineering of PbSe Nanowires to Construct Electronic and Optoelectronic Devices





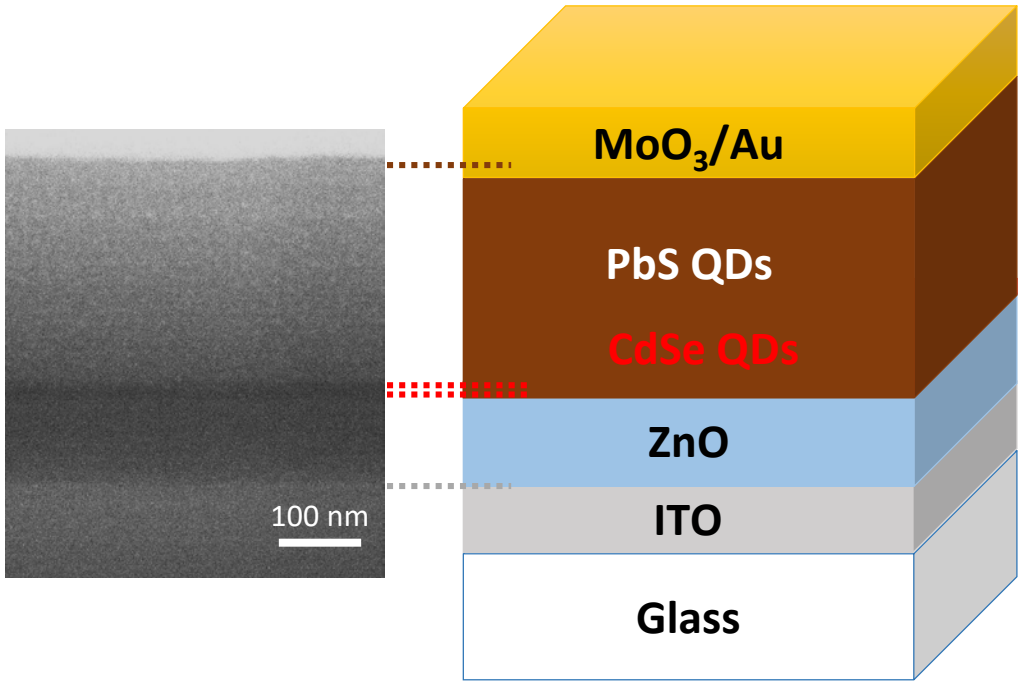


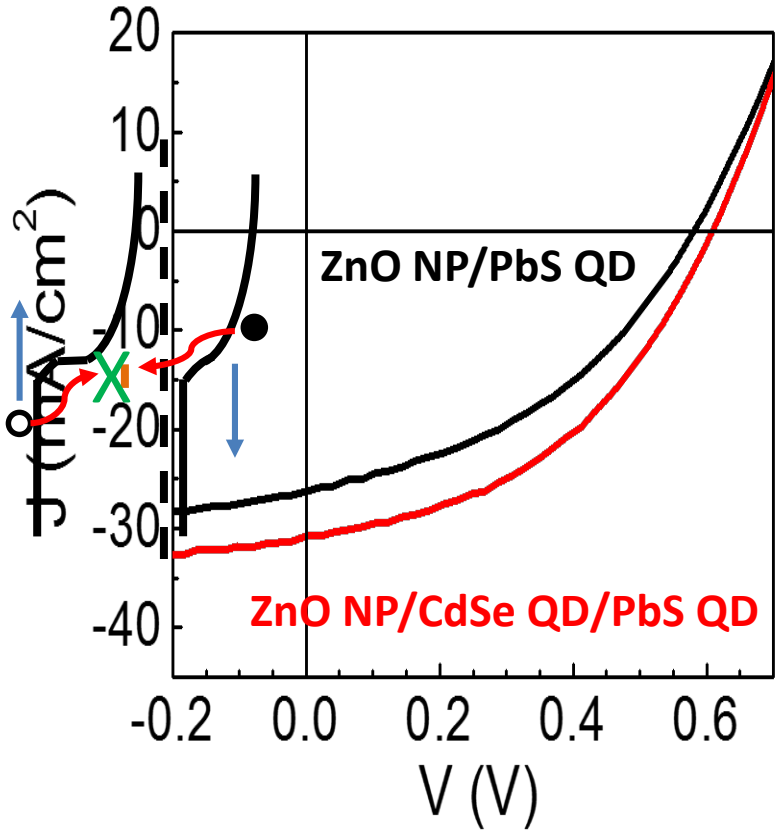


*Oh, Uswachoke, Zhao, Choi, Diroll, Murray, Kagan, ACS Nano, **9**, 7536 (2015).*

Advanced Architecture for Colloidal PbS Quantum Dot Solar Cells

Sargent, Alivisatos, Bawendi/Bulovic, Luther/Beard, Nozik ….

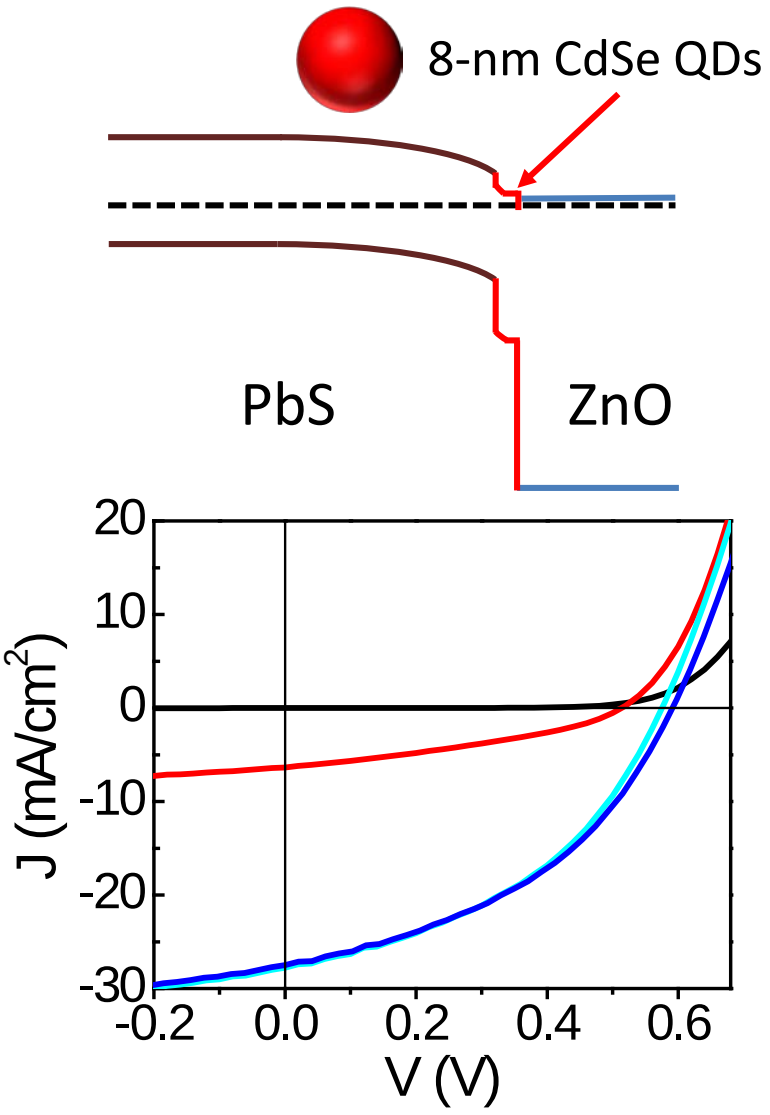


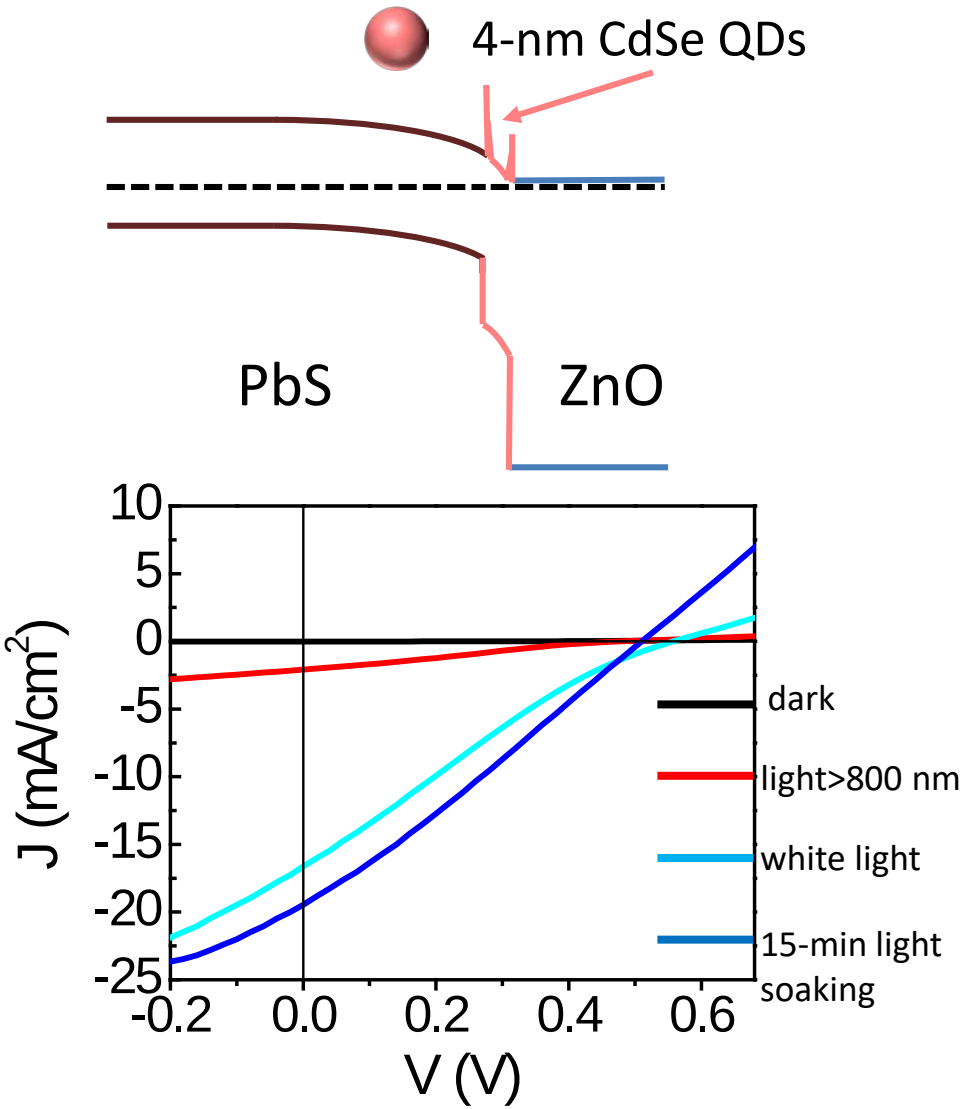


N=20	Voc (V)	Jsc (mA/cm²)	FF	PCE (%)
ZnO NP/PbS QD	0.586±0.017	25.0±1.8	0.41±0.03	6.0±0.5
ZnO NP/CdSe QD/PbS QD	0.600±0.017	29.5±2.0	0.43±0.02	7.5±0.4

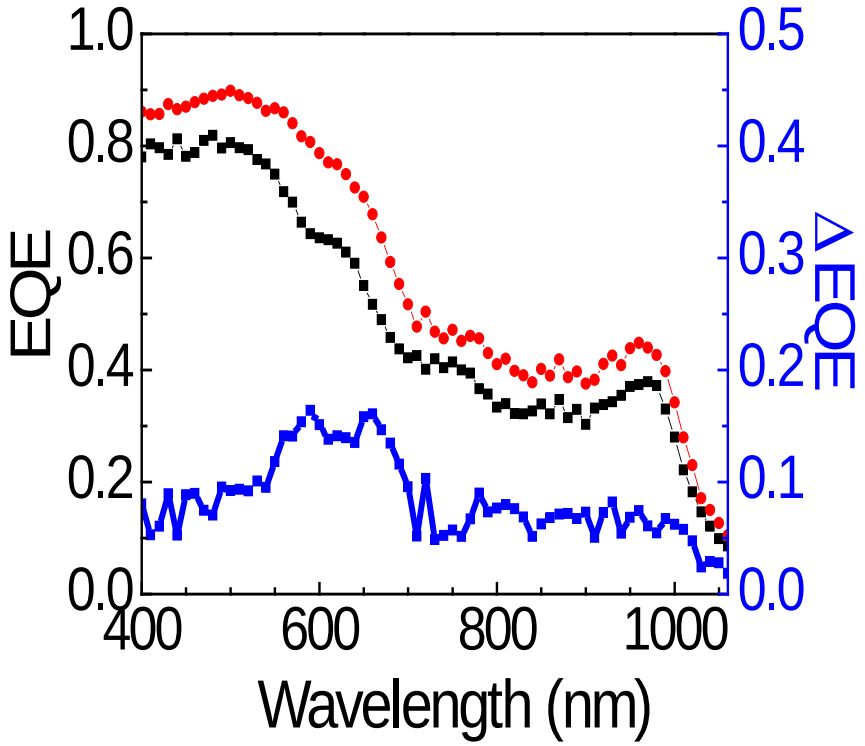
*Zhao, Goodwin, Guo, Wang, Diroll, Murray, Kagan, ACS Nano, **10**, 9267 (2016).*

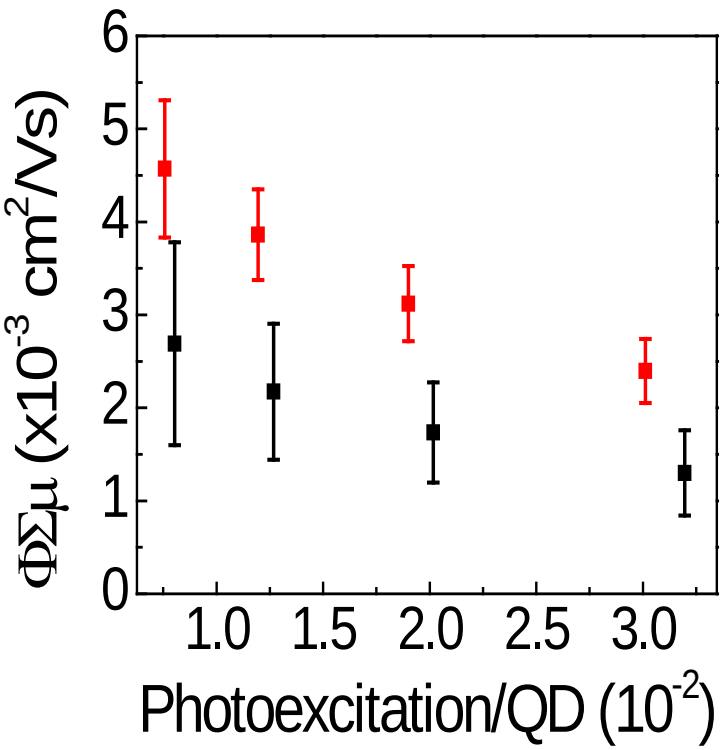
Band Gap Engineering of QD Solar Cells





PbS Quantum Dot Solar Cell Performance Enhancement





reduce interface recombination and increase photogeneration

Conclusions

1. synthesis of monodisperse nanocrystals
2. exchange long surface ligands used in synthesis for compact ligands
3. passivate surface traps and remotely dope NC solid
4. engineer device interfaces

to design the carrier mobility and lifetime of NC solids